VOLUME 62, NUMBER 6 PHYSICAL REVIEW LETTERS 6 FEBRUARY 1989

Resistivity of Strong-Scattering Alloys: Absence of Localization and Success of Coherent-Potential Approximation Confirmed by Exact Supercell Calculations in $V_{1-x}Al_x$

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(Received 27 September 1988)

A supercell procedure for exact evaluation of the one-electron Kubo-Greenwood formula is applied to the resistivity ρ of $V_{1-x}Al_x$ alloys and compared with a Korringa-Kohn-Rostoker coherent-potential approximation calculation. The results of these calculations agree well, consistent with the observation of delocalized eigenstates, in spite of the very high resistivity, $\rho \approx 200\ \mu\Omega$ cm.

PACS numbers: 72.15.Eb, 71.20.Ad, 71.55. Dp

There are many unresolved questions concerning the resistivity ρ of strong-scattering metals and alloys. Two examples are the reason for high-temperature resistivity saturation[1] and the explanation of the Mooij correlation between the sign of the temperature coefficient of resistance, given by $(1/\rho)(d\rho/dT)$, and the resistance magnitude.[2] Both effects lie outside the standard quasiparticle (Bloch-Boltzmann) picture. Korringa-Kohn-Rostoker band theory and coherent-potential approximation (KKR and CPA, respectively)[3] give a systematic scheme which improves on the Boltzmann equation (Butler [4] has shown how to add the ladder-type vertex corrections which generate the "scattering in" term). However, it is difficult to take this procedure beyond the single-site approximation. Thus Anderson ("strong") localization cannot be incorporated, because it depends on scattering from clusters of atoms. But localization of the "weak"[5] and "strong"[6] forms has been invoked to explain both of the phenomena mentioned above. The main purpose of the present paper is to show that large supercell calculations, which can incorporate strong localization, can be realistically applied to the problem of resistivity of "strong scattering" (mean free path $l < 10$ Å) d-band alloys. A second purpose is to argue that for the specific case of $V_{1-x}Al_x$ alloys, localization effects are not important. A third purpose is to show that KKR CPA resistivity theory is remarkably successful in this strong-scattering situation. This complements earlier work[7] where it was shown that KKR CPA worked well for resistivity of nondilute alloys with $l > 10$ Å.

The $V_{1-x}Al_x$ system was chosen because it has a substitutional bcc structure for $x < 0.4$ and very large[8,9] ρ ($> 200\ \mu\Omega$ cm near $x = 0.4$). For four choices of x, KKR CPA equations were solved self-consistently and ρ was calculated from Butler's formulas.[4] Self-consistent potentials $v(\mathrm{V})$ and $v(\mathrm{Al})$ were taken from each KKR CPA calculation and used in a non-self-consistent fashion to solve exactly the linearized KKR equations for large cells of up to 240 primitive bcc cells. The site occupancy was chosen to be V or Al at random, consistent with the chosen value of x. Only the $k = 0$ point of the supercell Brillouin zone was sampled (identical to a cluster calculation with periodic boundary conditions). The resulting eigenfunctions $|i\rangle$ and energies ϵ_i are used directly in the Kubo-Greenwood formula,[10] which is exact in one-electron approximation:

$$\sigma(\omega) = \frac{\pi e^2 \hbar}{N \Omega m^2} \left\langle \sum_{ij} \left| \langle i | p_x | j \rangle \right|^2 \frac{f_i - f_j}{\epsilon_j - \epsilon_i} \delta(\hbar\omega - \epsilon_j + \epsilon_i) \right\rangle . \tag{1}$$

Here p_x is the momentum operator in the x direction, f_i is the Fermi function for state i, Ω is the atomic volume, and N is the number of atoms. Ensemble averaging (indicated by the angle brackets) is approximated by averaging over five independent random configurations for each x.

Two technical difficulties deserve mention. One is momentum matrix elements, which place heavier demands on wave-function accuracy than do energy eigenvalues. We have included angular basis functions out to $l = 3$ on both Al and V atoms, even though $l = 1$ (for Al) and $l = 2$ (for V) gives reasonably good energies. Even these choices do not converge $\langle i | p_x | j \rangle$ perfectly, as will be explained later. Second, the sums in Eq. (1) are well defined only for the infinite volume limit where the spectrum is continuous. For a sample with 200 atoms the mean level separation at ϵ_F is ~ 3.4 meV or 40 K, and it is necessary to use a broadened δ function, with a width greater than the level spacing. Since there is no sharp structure on this scale, this creates no difficulties. Somewhat more difficult is the fact that statistical errors in $\sigma(\omega)$ get large as $\omega \rightarrow 0$ because the number of particle-hole pairs near ϵ_F with small $\epsilon_j - \epsilon_i$ goes to zero as $\hbar\omega = \epsilon_j - \epsilon_i$ goes to zero. Again, the absence of sharp structure is helpful. A parabolic fit $\sigma(\omega) = \sigma(0) - a\omega^2$

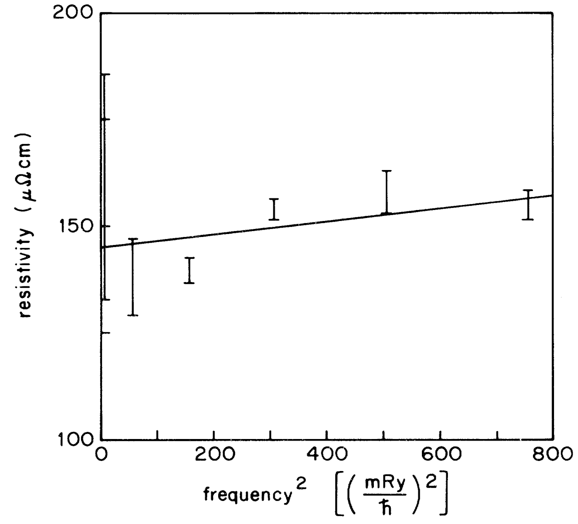

FIG. 1. The resistivity vs the square of the frequency for $V_{0.68}Al_{0.32}$. The vertical bars represent statistical 86% confidence limits.

in the interval $\hbar\omega < 0.5$ eV gives an extrapolated $\sigma(0)$ accurate to within 10%. A typical case is shown in Fig. 1.

Figure 2 gives results for a particular 120-atom supercell of $V_{0.68}Al_{0.32}$. There is remarkably good agreement between the exact density of states and KKR CPA values. The eigenstates are tested for localization by a calculation of the participation ratio $P(i)$ defined as

$$P(i)=\left[N\sum_{\mathbf{R}}|\langle\mathbf{R}|i\rangle|^4\right]^{-1}, \tag{2}$$

where $\langle\mathbf{R}|i\rangle$ is the projection of the eigenstate i on site $\mathbf{R}$. $P(i)$ equals 1 for a completely extended state, $1/N$ for a state restricted to a single atom, and approximately M/N for a state extended over M atoms in the supercell. In Fig. 2, values of $P(i)$ are > 0.4 for all states near E_F, showing that no localization occurs, at least on length scales comparable to or smaller than our cell size. The eigenstates are extended but nonpropagating, with little remnant of a **k**-vector and thus no way to define a velocity or mean free path.

Figure 3 shows resistivities calculated by both supercell and KKR CPA procedures. The two theories agree well but lie systematically below experiment by ~40%. Since the supercell procedure represents an exact solution (with < 10% statistical error) of the model which KKR CPA attempts to solve, we conclude that KKR CPA does a remarkably good job in this case.

There are several possible explanations for the discrepancy with experiment. Our theory uses local-density approximation outside the sphere where density-functional theory technically applies[11]: Resistivity is a nonequilibrium process involving excited states while density-functional theory deals in equilibrium properties.

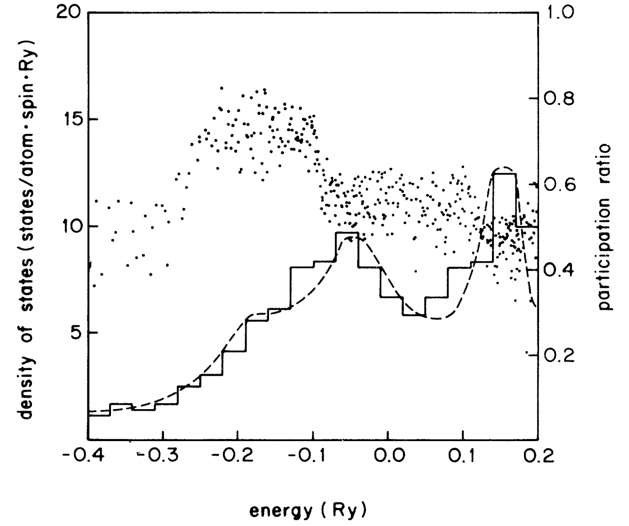

FIG. 2. The participation ratio for each state from a single 120-atom supercell calculation in the relevant energy range (dots), the KKR CPA density of states (dashed line), and the supercell density of states (solid histograms) vs energy for randomly disordered $V_{0.68}Al_{0.32}$. The energy zero is the Fermi energy.

Experiment suggests that local-density approximation band theory often provides a successful model for excitations in d-band metals (for example, resistivities[12] of elements are understandable this way). This success has no fundamental basis, and may fail here (for example, disorder can enhance quasiparticle interactions[13]). Before affirming such a conclusion, we must examine all other

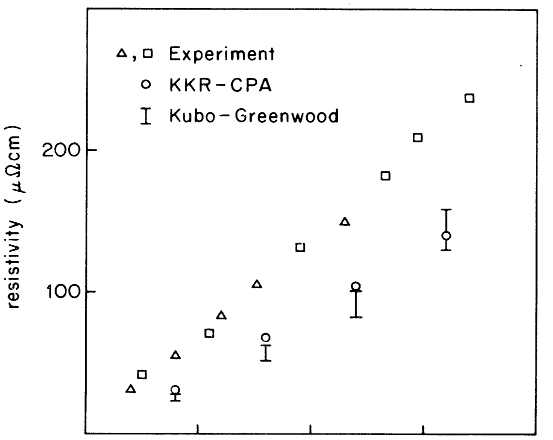

FIG. 3. The experimental (squares, Ref. 9; triangles, Ref. 8), KKR CPA (circles), and supercell (vertical bars) resistivity for randomly disordered $V_{1-x}Al_x$ alloys vs concentration. The vertical bars represent approximate 90% confidence limits.

approximations which could contribute. Five possible sources of error with our local-density approximation treatment are (a) static displacements of atoms from bcc sites, (b) deviations from random site occupancy, (c) additional scattering from larger clusters, (d) nonconvergence of $\langle i | p_x | j \rangle$, and (e) "shape" approximations on the potential.

(a) We have ignored static distortions from perfect bcc sites which are a possible source of extra resistance. Because the size mismatch of V and Al atoms is only ~6%, the effect should not be big. Consider a 5% solution of Al in V with Al atoms isolated. The eight nearest-neighbor V atoms should displace ~0.05 Å, while second neighbor displacements are smaller and partially canceled by competing effects of several impurities. If every V atom had a random displacement of 0.05 Å, this would enhance the resistivity by ~4, $\mu\Omega$ cm. This estimate comes from observing that the room-temperature resistivity of pure V, 23 $\mu\Omega$ cm, arises from rms thermal displacements of ~0.12 Å, and assuming that resistivity scales as the mean-square displacement. Since only 40% of the atoms are displaced in $V_{0.95}Al_{0.05}$, we expect $\Delta\rho < 2$ $\mu\Omega$ cm, which is ~5% of the observed residual resistance of 40 $\mu\Omega$ cm. At higher Al concentrations, the effect is probably smaller than 5%.

(b) Short-range order, which is beyond the reach of CPA, is easily incorporated in a supercell. New cells have been created with local ordering biased by use of several choices of a pair interaction U (defined as $2U_{ab} - U_{aa} - U_{bb}$, where U_{ab} is the "strength" of an ab bond). The degree of bias is measured by the short-range-order parameter $S = 1 - P_{ab}/2C_aC_b$ where P_{ab} is the probability that an arbitrary bond is an ab bond, and C_a is the concentration of component a. Figure 4 shows our results. The ordering coefficient $(1/\rho)(d\rho/dS)$ is small, in the range $(-1.4, 0.6)$. The extreme case of -1.4 requires a substantial amount of ordering, $S = -0.3$, to enhance ρ by 40%. Since S is bounded below by $-x/(1-x)$, a value $S = -0.3$ can only be achieved for $x > 0.2$. It seems likely that ordering is not the explanation. It would be helpful if S were known experimentally.

(c) We estimate that additional scattering from larger clusters is small, almost certainly less than 10%. Weak localization ideas[14] suggest that excess resistivity coming from clusters larger in size than L should be suppressed by inelastic scattering when the inelastic diffusion length $l_i(T) = [D\tau_i(T)]^{1/2}$ is less than L. Experimentally a 6% decrease of $\rho(T)$ is seen between 0 and 300 K in a sample with $x = 0.34$. By 300 K $l_i(T)$ is surely smaller than our 15-Å cell size (in pure V at 300 K, the inelastic mean free path is only 25 Å). Thus a maximum enhancement of 6% is expected at large x. The close agreement between KKR CPA and supercell methods also suggests that excess ρ from correlated scattering is a small effect.

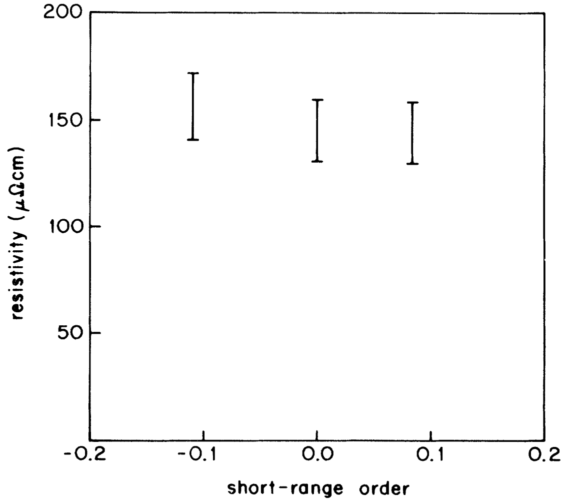

FIG. 4. The calculated supercell (vertical bars) resistivity vs short-range order for $V_{0.68}Al_{0.32}$. The vertical bars represent approximate 90% confidence limits.

(d) Momentum matrix elements have been handled in exactly the same way in both supercell and KKR CPA calculations. If we had overestimated these matrix elements by 18%, this would have underestimated the resistivity by 40%. As a test, we examined the accuracy of the diagonal matrix element $\langle \mathbf{k}n | p_x | \mathbf{k}n \rangle$ for crystalline V, compared with the exact answer $d\epsilon/d(\hbar k_x)$ for various bands at four points along the (100) direction. The root-mean-square discrepancy, 12%, is a measure of the truncation error in the angular basis. Thus accurate comparison with experiment will require an $l = 4$ basis, but the expected error with $l = 3$ seems a little smaller than our 40% discrepancy.

(e) The final error comes from forcing the potential to be either $v(\mathrm{Al})$ or $v(\mathrm{V})$ (and of muffin-tin form) rather than allowing complete relaxation of charge. Although complete self-consistency is in principle possible by supercell techniques, it is a little beyond present capabilities and does not seem likely to introduce major changes in ρ. As a test, we arbitrarily shifted the flat part of $v(\mathbf{r})$ outside the muffin-tin radius by ±20 mRy inside V cells relative to the value inside Al cells. This had little influence on ρ.

In conclusion, a supercell method is well suited to study resistivity of alloys with very short mean free paths. We find no evidence for incipient strong localization in a very resistive alloy, $V_{1-x}Al_x$, and excellent success of KKR CPA. It is premature to identify firmly the source of the 40% discrepancy with experiment.

We thank J. C. Swihart for invaluable assistance with the KKR CPA calculations. The work of P.B.A. was supported in part by the Division of Materials Sciences, U.S. Department of Energy, under Contract No. DE-AC02-76CH00016. The work of R.H.B. was supported in part by National Science Foundation Grant No. DMR84-20708. The work of D.M.N. and W.H.B. was sponsored by the Division of Materials Sciences, U.S. Department of Energy under Contract No. DE-AC05-84OR-21400 with Martin Marietta Energy Systems Inc. The large matrix calculations were done at the Cornell National Supercomputer Facility.

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